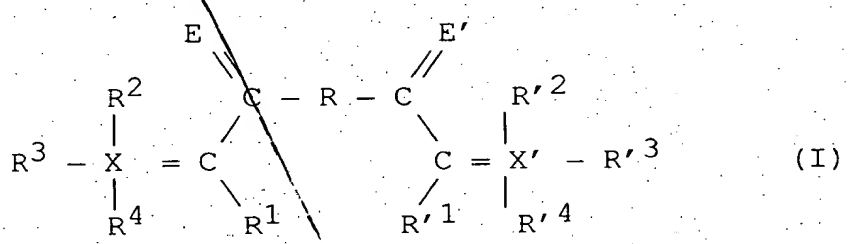
CLAIMS

1 - A catalytic system characterized in that it consists of:

(A) at least one ligand which can be represented by the general formula (I):



(I)

where:

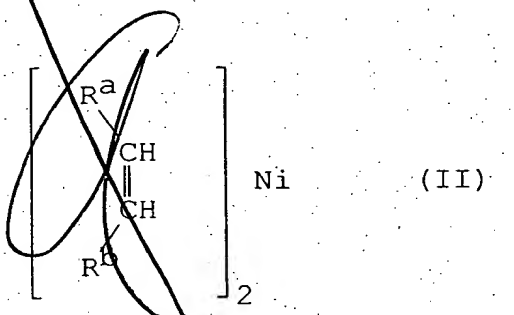
- E and E′ each represent independently an oxygen or a sulfur atom;
- X and X′ each represent independently a phosphorus, arsenic or antimony atom;
- the radicals R^1 and R'^1, which may be identical or different, are chosen from:
  - . hydrogen;
  - . linear, branched or cyclic alkyl radicals;
  - . aryl radicals;
  - . arylalkyl radicals;
  - . alkylaryl radicals;
  - . halogens;
  - . the hydroxyl radical;
  - . alkoxide radicals;
  - . $-\overset{\overset{O}{\|}}{C}-OR'$, where R′ represents a hydrocarbon radical which may have from 1 to 15 carbon atoms;
  - . $-SO_3Y$, where Y is chosen from Li, Na, NH_4^+, $NR''_4{}^+$ (where R″ represents a hydrocarbon

radical which may have from 1 to 15 carbon atoms);

- the R^2, R'^2, R^3, R'^3, R^4 and R'^4 radicals, which may be identical or different, are chosen from linear, branched or cyclic alkyl radicals, and arylalkyl radicals;
- R is a divalent radical; and

(B) at least one nickel compound chosen from:

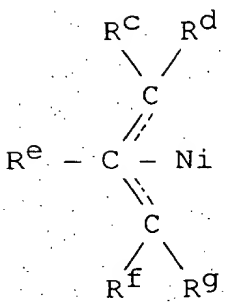
(B1) nickel complexes with a zero oxidation state, which can be represented by the general formula (II):



(II)

where R^a and R^b each represent independently a hydrogen atom, or a linear, branched or cyclic alkyl radical or aryl, arylalkyl or alkylaryl radical, which may have up to 8 carbon atoms, it being possible for R^a and R^b to form together a divalent aliphatic group of 2 to 10 carbon atoms and be able to have up to three olefinic double bonds as the only carbon-carbon unsaturated groups;

(B2) π-allylnickels, which can be represented by the general formula (III):

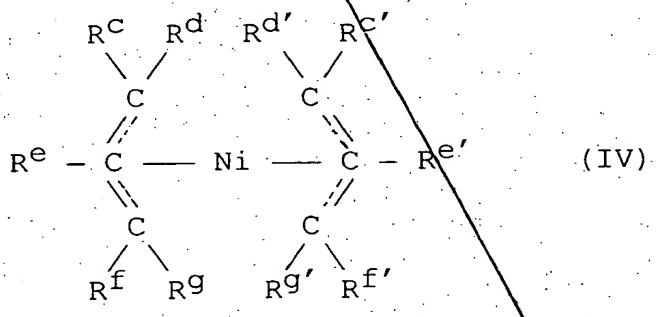


(III)

in which:

- the R^c, R^d, R^e, R^f and R^g radicals, which may be identical or different, are chosen from hydrogen, linear, branched or cyclic alkyl radicals and aryl, arylalkyl or alkylaryl radicals, having up to 8 carbon atoms;
- the dotted lines represent the electron delocalization on the three contiguous carbon atoms;
- an R^c or R^d radical may form, with an R^e or R^f or R^g radical, a divalent alkene group having from 2 to 10 carbon atoms and able to have up to three olefinic double bonds; and
- Z represents a halogen, an alkoxy group or an alkanoyloxy group;

(B3) compounds of the bis(allyl)nickel type which can be represented by the general formula (IV):



(IV)

in which:

- the radicals R^e to R^g, and $R^{e'}$ to $R^{g'}$, which may be identical or different, are chosen from hydrogen, linear, branched or cyclic alkyl radicals and aryl, arylalkyl or alkylaryl radicals having up to 8 carbon atoms;
- the dotted lines represent the electron delocalization on the three contiguous carbon atoms;
- a radical R^c or R^d able to form, with a radical R^e or R^f or R^g, a divalent alkene group having from 2 to 10 carbon atoms and able to have up to three olefinic double bonds;
- a radical $R^{c'}$ or $R^{d'}$ able to form, with a radical $R^{e'}$ or $R^{f'}$ or $R^{g'}$, a divalent alkene group having from 2 to 10 carbon atoms and able to have up to three olefinic double bonds.

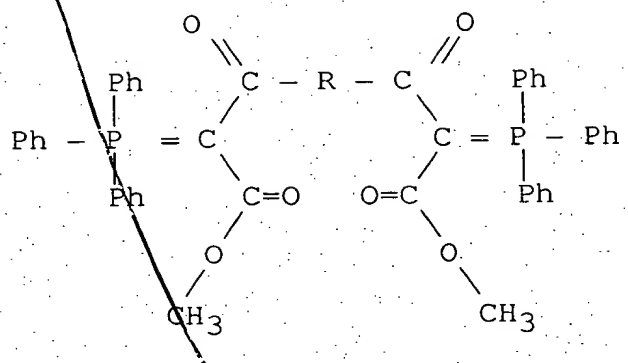
2 - The catalytic system as claimed in claim 1, characterized in that, in formula (I), E and E′ are separated by intermediate atoms linked together by covalent or coordinate bonds.

3 - The catalytic system as claimed in either of claims 1 and 2, characterized in that, in formula (I), the minimum number of atoms between E and E′ is from 3 to 40.

4 - The catalytic system as claimed in either of claims 1 to 2, characterized in that, in formula (I), R is chosen from:

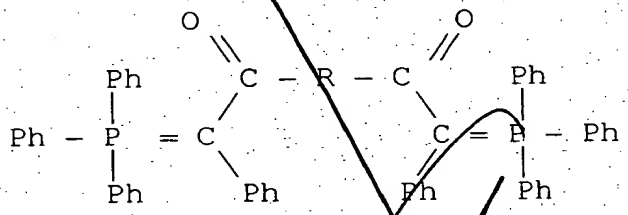
- divalent hydrocarbon radicals comprising from 2 to 38 carbon atoms; and
- the 1,1'-ferrocenylene radical which may be substituted.

5 - The catalytic system as claimed in one of claims 1 to 4, characterized in that the ligand of formula (I) comprises one of the following structures:



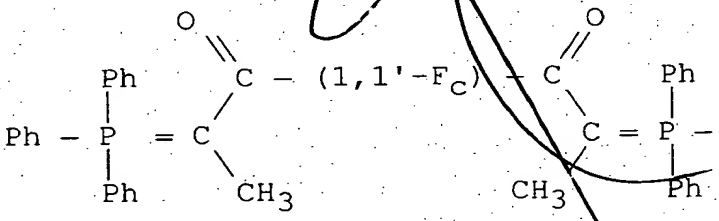
(Ia)

where R represents a 5,6-bicyclo[2.2.1]hept-2-ene radical; $-(CH_2)_4-$ or $-(CH_2)_8-$;



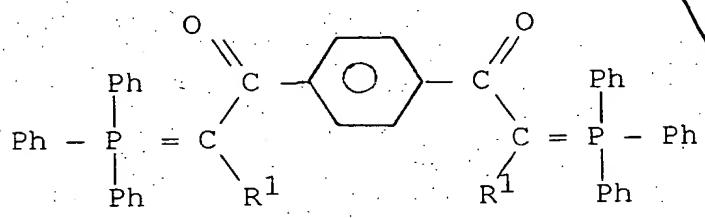
(Ib)

where R represents a 5,6-bicyclo[2.2.1]-hept-2-ene radical; or $-(CH_2)_8-$;



(Ic)

where 1,1'-F_c represents a-1,1'-ferrocenylene radical; and



(Id)

where R^1 represents H or Ph or SO_3Na or $-C(=O)-O-CH_3$.

6 - The catalytic system as claimed in one of claims 1 to 5, characterized in that the nickel compound (B_1) is chosen from:

. bis(1,5-cyclooctadiene)nickel(0);
. bis(cyclooctatetraene)nickel(0); and
. bis(1,3,7-octatriene)nickel(0).

7 - The catalytic system as claimed in one of claims 1 to 5, characterized in that, in a nickel compound (B2) or (B3), a π-allyl group has from 3 to 12 carbon atoms which do not have other aliphatic unsaturated groups, except where it contains a closed cycle.

8 - The catalytic system as claimed in one of claims 1 to 5, characterized in that the nickel compound (B2) is chosen from:

. π-allylnickel chloride;
. π-allylnickel bromide;
. π-crotylnickel chloride;
. π-methylallylnickel chloride;
. π-ethylallylnickel chloride;
. π-cyclopentylallylnickel bromide;
. π-cyclooctenylnickel chloride;
. π-cyclooctadienylnickel chloride;
. π-cynnamylnickel bromide;
. π-phenylallylnickel chloride;
. π-cyclohexenylnickel bromide;
. π-cyclododecenylnickel chloride;
. π-cyclododecatrienylnickel chloride;
. π-allylnickel acetate;
. π-methylallylnickel propionate;
. π-cyclooctenylnickel octoate;
. π-cyclooctenylnickel methoxylate; and
. π-allylnickel ethoxylate.

9 - The catalytic system as claimed in one of claims 1 to 8, characterized in that the nickel compound (B3) is chosen from:

. bis(π-allyl)nickel;
. bis(π-methallyl)nickel;
. bis(π-cynnamyl)nickel;

. bis(π-octadienyl)nickel;
. bis(π-cyclohexenyl)nickel;
. π-allyl-π-methallylnickel; and
. bis(π-cyclooctatrienyl)nickel.

10 - The catalytic system as claimed in one of claims 1 to 9, characterized in that the components (A) and (B) are present in amounts such that the nickel-to-ligand(s) molar ratio is between 1 and 100.

11 - The catalytic system as claimed in claim 10, characterized in that the components (A) and (B) are present in amounts such that the nickel-to-ligand(s) molar ratio is between 2 and 50.

12 - A process for the polymerization of at least one olefin in the presence of a catalytic system as defined in one of claims 1 to 11.

13 - The process as claimed in claim 12, characterized in that:

- in a first step, each of the constituents (A) and (B), which are in solution in an inert solvent, are introduced separately or simultaneously into a reactor, together with the reaction mixture; and
- in a second step, the olefin or olefins are introduced, the (co)polymerization taking place at a temperature between 0 and 300°C and at a total absolute pressure of from 1 to 200 bar.

14 - The process as claimed in claim 13, characterized in that the constituents (A) and (B) are introduced in a nickel-to-ligand(s) molar ratio of between 1 and 100.

15 - The process as claimed in claim 14, characterized in that the constituents (A) and (B) are introduced in a nickel-to-ligand(s) molar ratio of between 2 and 50.

16 - The process as claimed in one of claims 13 to 15, characterized in that the inert solvent of constituents (A) and (B) is chosen from saturated aliphatic hydrocarbons, saturated alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof.

17 - The process as claimed in one of claims 13 to 16, characterized in that the reaction mixture consists of an organic medium.

18 - The process as claimed in claims 13 to 16, characterized in that the reaction mixture comprises a continuous liquid aqueous phase, which comprises more than 30% water by weight.

19 - The process as claimed in claim 18, characterized in that the aqueous phase is the only liquid phase.

20 - The process as claimed in claim 18, characterized in that the mixture comprises an organic liquid phase.

21 - The process as claimed in one of claims 17 and 20, characterized in that the medium or the organic phase is chosen from:

- saturated aliphatic hydrocarbons, saturated alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof; and
- to the extent that the polymerization conditions keep them in liquid form, α-olefins, unconjugated dienes and mixtures thereof.

22 - The process as claimed in one of claims 18 to 21, characterized in that the polymerization medium comprises a dispersing agent.

23 - The process as claimed in claim 22, characterized in that the dispersing agent is present at up to 10% by weight with respect to the weight of water, in particular, at 0.01 to 5% by weight, with respect to the weight of water.

24 - The process as claimed in one of claims 18 to 23, characterized in that the polymerization medium comprises an emulsifying agent.

25 - The process as claimed in claim 24, characterized in that the emulsifying agent is present at up to 10% by weight, in particular at 0.01 to 5% by weight, with respect to the weight of water.

26 - The process as claimed in either of claims 24 and 25, characterized in that the emulsifying agent is present in an amount greater than the critical micelle concentration.

27 - The process as claimed in claim 26, characterized in that the amount of emulsifying agent is enough so that the polymerization takes place mainly in the micelles.

28 - The process as claimed in one of claims 24 to 27, characterized in that the polymerization medium comprises a liquid organic phase and a cosurfactant.

29 - The process as claimed in claim 28, characterized in that the polymerization mixture comprises a liquid organic phase and a cosurfactant.

30 - The process as claimed in claim 29, characterized in that the cosurfactant has a solubility in water of less than 1×10^{-3} mol per liter at 20°C.

31 - The process as claimed in either of claims 29 and 30, characterized in that the cosurfactant is present at up to 10% by weight with respect to the weight of water.

32 - The process as claimed in one of claims 29 to 31, characterized in that the emulsifying agent to cosurfactant mass ratio goes from 0.5 to 2.

33 - The process as claimed in one of claims 13 to 32, characterized in that the concentration of the constituent (A) in the inert solvent is between 0.1 micromol and 100 millimol per liter of solution.

34 - The process as claimed in one of claims 13 to 33, characterized in that the concentration of the constituent (B) in the inert solvent is between 0.1 micromol and 200 millimol per liter of solution.

35 - The process as claimed in one of claims 13 to 34, characterized in that it is carried out in an inert atmosphere.

36 - The process as claimed in one of claims 13 to 35, characterized in that, in a preliminary step, the constiuents (A) and (B) in solution are brought into contact with each other in their inert solvent, for a duration of 30

seconds to 10 minutes, before their introduction into the reaction mixture.

37 - The process as claimed in claim 36, characterized in that this precontacting step is carried out in an inert atmosphere, at a temperature of between 0 and 100°C, in particular between 10 and 70°C.

38 - The process as claimed in one of claims 13 to 35, characterized in that the constituents (A) and (B), which are in solution in their inert solvent, are introduced separately into the reaction mixture, the latter being held at a temperature of from 0 to 100°C, in particular from 10 to 70°C.

39 - The process as claimed in one of claims 13 to 38, characterized in that the (co)polymerization is carried out at a temperature of between 25 and 200°C.

40 - The process as claimed in one of claims 13 to 39, characterized in that the (co)polymerization is carried out at a total absolute pressure of from 1 to 100 bar.

41 - The process as claimed in one of claims 13 to 40, characterized in that the olefin or olefins intended to be polymerized are introduced in gas or liquid form, with enough stirring of the polymerization medium, in particular with stirring ranging from 10 to 10 000 revolutions per minute.

42 - The process according to one of claims 13 to 41, characterized in that the olefins are chosen from ethylene, α-olefins, cyclic olefins and compounds of formula:

$$CH_2=CH-(CH_2)_n-G-$$

in which:

- n is an integer between 2 and 20; and
- G is a radical chosen from:
  -OH; $CHOHCH_2OH$; OT; $-CF_3$; -COOT; -COOH;
  $-Si(OH)_3$; $-Si(OT)_3$;
  T is a hydrocarbon radical having from 1 to 20 carbon atoms.

43 - The process as claimed in one of claims 13 to 41, characterized in that at least one olefin is ethylene.

44 - The process as claimed in one of claims 24 to 43, characterized in that it leads to a latex, if necessary after a filtration step.

45 - The process as claimed in claim 44, characterized in that the latex is a high-density polyethylene or a medium-density polyethylene or a low-density polyethylene.

Add A1

add D27